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Plastics

Dealing with the Manufacture, Uses and Potentialities of Plastic Materials

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The New Year

WITH the passing of the old year, a year of building up and co-ordinating our resources and forces, at the same time resisting the attacks of the enemy, we enter a New Year rapidly approaching our peak in production, a year in which we shall commence our great assaults on the evil foe. As Mr. Churchill has put it, Britain is a tough chicken with a very tough neck, not easy to wring. It is now a fighting cock and we have been able to fit it with spurs, the points of which the Germans will soon feel. These spurs have been hammered sharp and tough in the workshops of the country, and it is the proud boast of the plastics industry that it has taken no small part in the doing of it.

To each and every factory, then, we offer our congratulations and our thanks. Theirs, no less than the sailors, soldiers and airmen, will be the victory. The light at the end of the tunnel approaches fast.

Plastics and Engineering

WE gave it as our opinion some years ago that the future of plastics will be brightest when technologists in the plastics industry are able to give papers before the learned societies of the engineering profession. The meaning of this, on analysis, becomes rather obvious, but it is none the less true and none the less heartening to our industry.

We all know that there have been many plastics introduced into the engineering industries, but the reading of a paper on the subject of plastics means that the materials have been tested and found not altogether wanting in the most exacting of all industries.

It is therefore with considerable pleasure that we have before us the lecture given by Dr. Caress at Newcastle before the North East Coast Institution of Engineers and Shipbuilders.

So far as they affected engineers, he said, plastics were just emerging from the status of accessories to that of light constructional materials, but with regard to the problem of replacing metals by organic solids it was not sufficient to consider the properties of existing plastics, but it was necessary to consider their limitations. Unfortunately, knowledge of the relationships between composition, structure and properties was not sufficiently advanced to give a quantitative answer, although qualitative generalizations could be made. Figures showed that the strength of metals was most nearly approached by the special fibre-reinforced phenol-formaldehyde, the next best being paper or fabric laminated p.f. It was, therefore, not surprising that those materials had made the greatest progress in engineering applications. The electrical engineering uses of phenol, cresol and aniline-formaldehyde laminated rod, tube and board in machined forms were well known.

Although plastics were first used as substitutes for wood, ceramics and metal, and latterly to supplement supplies of metals, there is a growing use of them, not as substitutes, but because they are specially adapted to the application, sometimes because they are the only possible materials for a novel use. Water-lubricated bearings and silent gears were familiar examples. Modern bomber and fighter aircraft depended for their streamlined cockpits and turrets on transparent methacrylate or acetate sheeting. When the war is over it would be possible to mention numerous new applications where light weight, electrical and chemical properties and ease of manufacture had pointed to one plastic or another as the only possible solution.

The greatest use of plastics in ships, in rail transport, etc., is still in the form of moulded articles, ranging from bathroom tiles and door furniture to ventilators and trays, although laminated veneers for table tops or panelling have also been introduced.

The use of plastics as constructional materials had received an impetus from the demand for saving in weight. That was one of the reasons why the aircraft industry was making greater use of plastics. Phenolic and urea resins were used, sometimes in combination with plywood, for the stressed-skin structure of wings and fuselages. The transparent parts of the aircraft shell were also subject to stress in service, and their low weight, as well as their ease of shaping, was an important factor in their use. Other industries would utilize those advantages, especially where weight saving was important, e.g., in cars, trains, ships and boats. One interesting example was the saving in weight which was said to have been made in the "Scharnhorst" by the use of extruded plastic insulation in place of the heavy, lead-covered cable previously employed.

The use of extruded plastics based on polyvinyl chloride and—where exceptionally low power loss was essential—polythene, as wire and cable insulation, was likely to spread to many industries. A specialized application of plastics, in which the density was further reduced artificially,

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was that of foamed resins in the thermal insulation of refrigerated ships' holds. Small craft had been made in synthetic-resin-bonded plywood, and canoes had been made by stretching plastic sheet (based on polyvinyl chloride) over wooden frameworks.

Among the mechanical uses of plastics, bearings and bushes made from phenolic laminated had been mentioned. Roll-neck bearings up to 30 ins. in diameter had been made for steel mills; the power consumption was reduced and water lubrication was possible. Nylon bearings were used in smaller sizes. Silent gears, clutches, pinions, etc., were further applications of laminated plastics. Moulded impellers, pump casings and fans were also used.

A considerable development of the use of plastics in chemical plant, tank wagons, etc., was to be expected. Corrosion-resistant tanks, vessels, valves, ducts and pipes were made from asbestos-filled phenolic plastics. Progress in Germany in the use of semi-rigid piping extruded from compositions based on polyvinyl chloride was likely to be followed here when the advantages of ease of jointing, resistance to attack and light weight were fully realized.

It was safe to predict that, in the normal course of development of existing plastics, uses in all branches of engineering would increase. Wherever a job could be done in wood it was probable that a better and more colourful job could be done by a combination of plastic and either wood itself or cellulose fibres in some other form. Already the all-plastics house was being mooted.

Another safe prediction was that the strongest and most stable of the transparent sheet plastics would find wider use as light structural materials. Glass itself was used to some extent in building construction, but the transparent thermoplastics had the advantages of being much less brittle, lighter, easier to shape and to machine.

The chemical engineer would also use extruded plastics, such as the more rigid compositions based on polyvinyl chloride, to solve corrosion problems which previously demanded special alloys. Simple welding and jointing methods would be employed in manipulating extruded tubes and sheets, and there would be a general trend towards adaptation of metal-working techniques.

This was a further extension of the use of plastics which did not involve any great improvement in the plastics themselves. That was the combination of plastics and other materials. The general usefulness of combinations of phenol-formaldehyde and cellulose had been noted already. Much greater use could be made of composite metal-plastics structures. In particular, it should be possible to utilize the great unidirectional fibre strength of the oriented plastics in that way.

PLASTICS AND METALS.—Dr. Caress continued by giving an interesting picture of the two fundamental differences between plastics and metals. The closer packing of metal atoms in a crystal where identical atoms were held together by undirected "metallic" bonds could be maintained when the atoms glided past one another—hence the ductility of metals. The three-dimensional plastics broke under pressure and were non-ductile; the primary bonds, which were directed, broke and could not be reformed. On the other hand, other forces in the plastic molecule were undirected and there was a better chance of their being restored, particularly if the long molecules were straight and parallel. Hence, the orientated thermoplastics showed some ductility.

The other difference arose from the loosely bound outer electrons in the metal atoms, giving metal electrical and thermal conductivity. Plastics were non-conductive, which gave them their great original importance, but the high thermal expansion was a disadvantage.

The strength of cellulose fibres appeared to approach the theoretical and the drawn synthetic polymer fibres similarly tended to the maximum possible strength. That was understandable, since the molecules were drawn out straight and parallel; if the sum of the secondary forces between the molecules was great enough (i.e., if the straight parts of the molecules were long enough), the material could only be broken by breaking primary bonds. From the picture of the structure of hardened phenol-formaldehyde it was equally understandable why its strength fell so far short of the maximum calculated strength as to be lower even than that of the stronger thermoplastics. That was so because the three-dimensionally bound lumps cemented together by residual forces could not be so well cemented as were straight parallel molecules. Uncontrolled cross-linking was thus in some respects worse than none; it did, however, increase resistance to solvents and to heat.

Again, if perfectly ordered cross-linking were possible, as in the diamond, would it produce a plastic constructional material superior to metals? It would be very hard and heat-resistant, but probably too brittle for general use, but not so brittle as unfilled phenol-formaldehyde. The answer would appear to be controlled cross-linking coupled with molecular orientation. Dr. Caress believed that progress along such lines would be achieved and that plastics would approach considerably nearer to metals in hardness, elasticity, toughness and strength.

SARAN.—The foregoing notes add considerable interest to the article on poly-vinylidene chloride, which we publish on another page. Here it is clearly shown how great is the increase in tensile strength on orientating the long molecules in more or less one direction by the method of extension. This is also the method employed in the technique of making nylon monofilament, and both nylon and Saran, which is the trade name for polyvinylidene chloride, have tensile strengths greater than some types of mild steel. It is also indicated in the article that Saran can be worked by methods similar to metal treatment.

We do not doubt that orientation can be carried out on all long-chain polymers, but also we must expect that, without cross-linkage, the simple long-chain polymers, although of great tensile strength, would tend to split along the "grain."

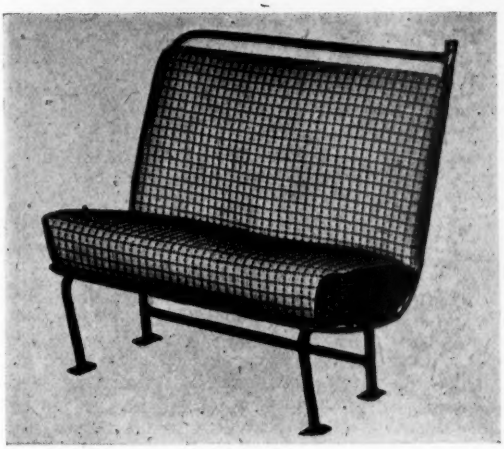
But we have also no doubt that future work, as Dr. Caress points out, will solve many mysteries and will give us that control over plastics so essential to our needs.

ECLIPSE OF TIN AND ALUMINIUM.—If all the face-cream and toothpaste-cream tubes made in one year were placed end to end they would reach to Heaven alone knows where. So it is especially pleasing to see the almost completely non-metallic tube recently issued by Herts Pharmaceuticals, Ltd., depicted herewith. It is a most interesting piece of work, for there are three mouldings: one, the cap, in black plastic; two, the black mushroom collar; and three, the white, threaded nozzle which continues as a

mushroom shape within. The black mushroom is screwed tightly over the white mushroom, holding firmly between them the tubular body. The latter consists of a plastic sheet lining, strongly protected on the outside by a fabric cover, probably artificial silk. The only metal part is the sealing strip at the bottom end. Altogether a very praiseworthy job, cleverly executed.

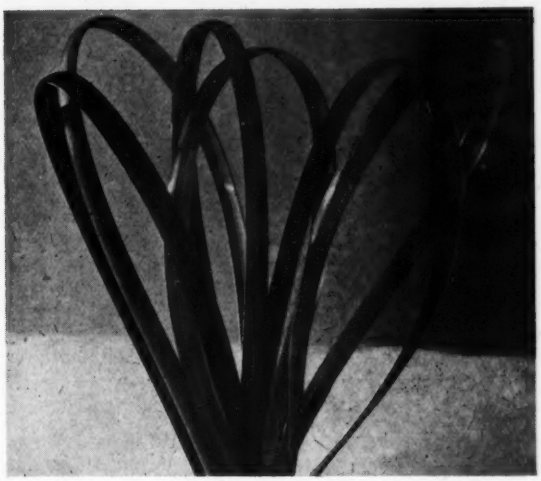
SAVE PAPER.—Paper is a munition of war for it is made into hundreds of different forms ranging from gun-cotton containers to medicine boxes for aircraft. So save it and keep on saving it.

SARAN—Vinylidene Chloride Polymers



Underground railway seat cover, fabricated in "plaited" Saran.

Extruded Saran of oval cross section as used for "wicker-work" seat covers.



Our readers may remember that in our September, 1941, issue on our Inquiries and Answers page we gave, in response to a question, some data regarding the new plastic polyvinylidene chloride. We have since received a letter from Mr. W. C. Goggin, Assistant Manager of the Plastic Sales Division of the Dow Chemical Company, Midland, Michigan, enclosing a copy of a paper read by him and R. D. Lowry, Research Supervisor of the Saran Development Laboratory, on September 10, 1941, before the American Chemical Society. Since few readers have an opportunity of obtaining original papers read abroad during war-time we have pleasure in abstracting it for publication.

By
W. C. GOGGIN
and
R. D. LOWRY

SOME 103 years ago the French chemist Regnault, in his studies[1] encountered a strange new fluid, which was later determined to be unsymmetrical dichloroethylene, now more commonly known as vinylidene chloride. From that time until the beginning of the past decade this material has rarely been in literature.

In 1922 B. T. Brooks[2] indicated that halogenated ethylenes, other than vinyl chloride and vinyl bromide, show a tendency towards polymerization. Staudinger and Feisst,[3] reporting in 1930 on the polymerization of an apparently impure unsymmetrical dichloroethylene, indicated that the liquid polymerizes quickly in light or slowly when kept in the dark. This polymeric material is completely saturated and its structure is represented by the long chain CH_2-CCl_2-CH_2-CCl_2-. Feisst reported the polymer to be crystalline.

The development of vinylidene chloride by the Dow Chemical Co. began actively over a decade ago and the first vinylidene-chloride polymers were produced in a commercial way early in 1940.

Chemical and Physical Structure

Vinylidene chloride has petroleum and brine for its basic raw materials. Ethylene gas, made by cracking petroleum, and chlorine gas, from the electrolysis of brine, combine to form trichloroethane, which is converted to vinylidene chloride, as shown in the accompanying flow sheet (Fig. 1). It is a clear, colourless liquid having a boiling point of 31.7 degrees C. and has the structural formula CH_2-CCl_2.

Vinylidene chloride can be readily polymerized to form the long, linear, straight-chain polymer, as portrayed in Fig. 2. By selection of copolymers and control of the polymerization conditions, polymers may be formed which have softening points ranging from about 70 degrees C. to at least 180 degrees C. Soft, flexible materials to hard, rigid materials can be obtained. Present commercial polymers have softening points from about 120 degrees C. to 140 degrees C. with a molecular weight of approximately 20,000. These polyvinylidene-chloride plastics are known by their trade name "Saran."

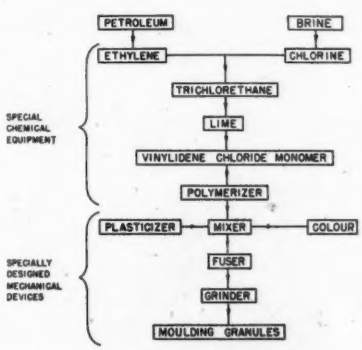


Fig. 1.—Flow sheet showing production of polyvinylidene polymers from petroleum and brine.

To a greater or lesser degree, Saran exhibits regions of crystal structure. This property can be demonstrated readily by its X-ray diffraction pattern. Most organic thermoplastics exist in an amorphous state and do not exhibit crystallinity. Under special conditions Saran can be made amorphous. When allowed to return to room temperatures, Saran gradually changes to its normal crystalline state. Amorphous Saran can be converted by mechanical working to an oriented crystalline state showing the lattice diffraction pattern. There are thus three physical conditions of Saran, amorphous, its normal crystalline unoriented state, and oriented.

General Properties

Saran can be obtained in a wide range of properties. For simplicity, a typical Saran formulation has been selected and its general properties are shown in Table 1. Specific properties of various fabricated forms will be discussed under the section on fabrication development.

One of the outstanding characteristics of Saran is its resistance to

TABLE 1
General Properties of a Saran Formulation

1. Effect of acids	None. (Strong H_2SO_4 darkens Saran.)
2. Effect of alkalis	None. Affected by strong ammonia. Darkens in strong caustic.
3. Effect of organic solvents ...	Highly resistant.
4. Water absorption	0.00%
5. Burning rate	None.
6. Thermal conductivity	2.2×10^{-4} cal./sec./sq. cm./°C./cm.
7. Specific heat	.316 cal./°C./gm.
8. Index of refraction	1.61
9. Specific gravity	1.70
10. Volume resistivity D.C. ...	10^{14}-10^{16} ohm cms.
11. Dielectric strength 60 cycles ...	500-2,500 volts/mil.
12. Dielectric constant 60 cycles ...	4
13. Power factor 60 cycles ...	.03-.08

chemicals and solvents. At room temperature it is extremely resistant to all acids and to all common alkalis, except for concentrated ammonium hydroxide. Slight discoloration with little change in mechanical properties will occur when exposed to concentrated sulphuric acid or caustic over long periods. It is substantially unaffected by both aliphatic and aromatic hydrocarbons, alcohols, esters, ketones and nitro-paraffins. It is swelled or softened only by oxygen-bearing organic solvents, such as cyclohexanone and dioxane. The resistance to chemicals or solvents decreases with a rise in temperature. The resistance of Saran to any chemical is in part a function of the crystallinity of the polymer. It is chemically more resistant in the crystallized form than in the amorphous state.

A second important characteristic of Saran is its extremely low water absorption and vapour transmission. According to A.S.T.M. test No. D570-40T over a period of 24 hrs., it shows a water absorption of 0.00 per cent. This low value accounts for its dimensional stability and freedom from warpage under a wide range of moisture exposure conditions. The low water vapour transmission or permeability of Saran is exemplified in the following test:—

A .001 in. thick Saran film tested in a Thwing-Albert vapometer at 45 degrees C. (113 degrees F.) transmitted only 1-3 gms./sq. m./24 hrs. These tests were run with the apparatus in dried recirculated air using water in the vapometer. This resistance to moisture transmission is at least five times that of the best commercially available organic film.

Saran is thermoplastic and has a definite softening point which limits the temperature at which it can be used. Since softening points vary with composition, the upper limit of operating temperature can be varied from 150 degrees F. to 250 degrees F. From the standpoint of fire hazard, exposures to much higher temperatures are not dangerous since Saran is non-inflammable.

The basic polymers are odourless, tasteless, and non-toxic. Their high refractive index enhances their many colour possibilities, while their toughness and abrasion resistance are of a high order, and the retention of these properties upon ageing insures excellent wearing qualities.

Fabrication Development and Applications

The fabrication of Saran presents many interesting problems. It can be fabricated by conventional thermoplastic practice, and, due to its normal crystalline state, it is susceptible to working by methods described later in this paper. In order to conserve the time and investment necessary for the fabricator to produce a finished product, as well as to supply a continually expanding background of technical service, the materials, processes, and equipment are being subjected to intensive study and development.

Saran is adapted to the conventional method for extrusion of plastics. Modified screw-type extrusion equipment is used. While these modifications are relatively minor, they are absolutely necessary for the successful extrusion of Saran. Designs permitting streamline plastic flow are desirable. Since iron and copper base metals catalyze the thermal decomposition of Saran in hot zones above 130 degrees C., it becomes necessary to select other suitable metals for these heated sections. The metals which can be used in contact with Saran above about 130 degrees C. are magnesium alloys, nickel, Z nickel, Hastelloy B, Stellite 10, and impervious hard chrome or nickel plate.

The extrusion of Saran includes supplying a uniform rate feed to the screw machine hopper, mixing and heating the plastic as it is forced along by the screw, and then forming it as it passes through the die. The extruded shape may be cooled and subsequently heat treated.

Saran may be fed to the extrusion unit as a powder or as granules. The powder presents no bulk problem with the screw machine and eliminates a costly milling operation. This powder, as originally manufactured, is conveniently and inexpensively plasticized, pigmented, and coloured by ball milling.

Thorough melting is of prime importance in the extrusion of Saran. To accomplish this, it is necessary to heat the material to above its crystallite melting point. In this condition, the product becomes completely amorphous.

Saran has a narrower softening range than most other thermoplastic

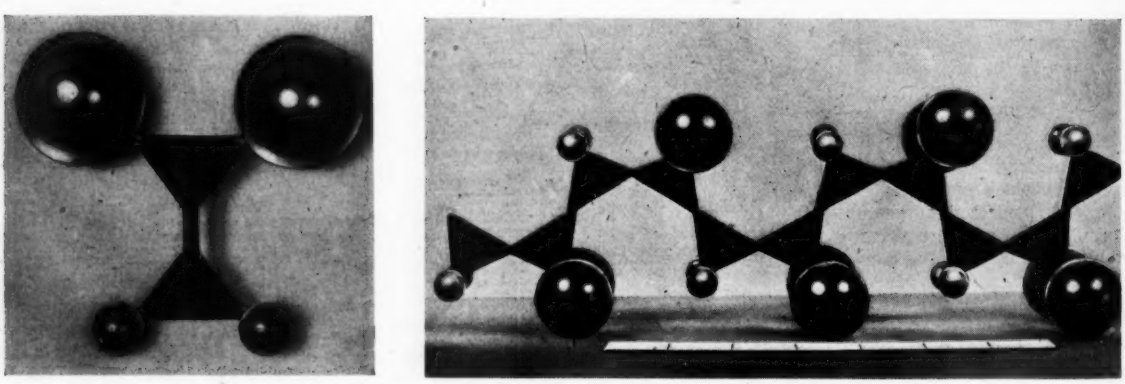


Fig. 2.—Theoretical conception of (left) the structural formula of the liquid monomer vinylidene chloride and (right) that of the polymer. The large spheres represent chlorine atoms and the small ones hydrogen. The interlinking tetrahedrons are carbon atoms.

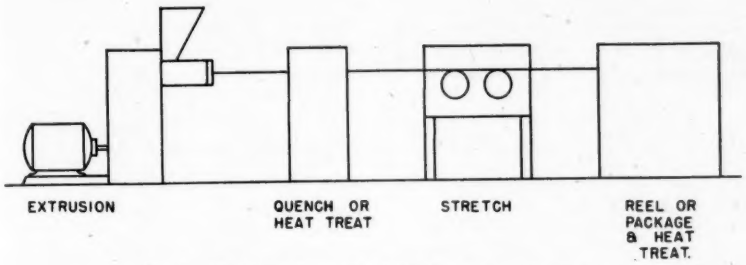


Fig. 3.—The extrusion and orientation process for Saran.

materials. When the material is heated above this narrow softening range it can be extruded in a very fluid state. Under these conditions, no plastic "memory" is encountered, thus making possible the retention of the desired shape and surface.

The product, when first extruded and cooled, is soft, weak, and pliable. If it is allowed to remain at room temperature without further treatment it will gradually harden while partially recrystallizing at a slow rate with a random crystal arrangement. By heat-treatment, recrystallization can be produced at controlled rates. Recrystallization time can be regulated from a few seconds to several weeks. For any one formulation, the rate of recrystallization is a function of the temperature. It is interesting to note that an increase in specific gravity occurs during recrystallization (S.G. changes from 1.66 to 1.69).

The control of extrusion and heat-treatment of Saran permits a range of properties to be obtained. Tensile strengths can thus be controlled from 4,000 lb./sq. in. to 12,000 lb./sq. in., hardness from 60 to 95 (Rockwell Superficial 15Y), elastic elongations from 10 per cent. to 40 per cent. Such products have good fatigue life as illustrated by the following example:—

Specimens of $\frac{5}{16}$-in. tubing having a wall thickness of $\frac{1}{16}$ in., when flexed through a 15-degree arc 1,750 times per minute for 2,500,000 cycles, are unruptured. In comparison, standard $\frac{1}{4}$-in. copper tubing failed after about 500 cycles in the same test.

A few of the applications of extruded Saran which appear of interest include: rods for making gaskets, valve seats, ball checks, medical probes; chemically resistant, flexible tubing and pipe; tape for wrapping joints; chemical conveyor belts; tape and strips for die cutting; and various items of wearing apparel.

Injection moulding offers a second fabrication method for Saran. This method makes possible the production of intricate shapes having properties similar to those obtained by extrusion as mentioned already. Here, again, the equipment involved consists of the standard conventional-type injection moulding machines modified only as to contact metal and designs through the heating tunnel or cylinder. The fundamentals of design include the same contact metals as listed for extrusion, strict streamlining, and the reduction of the thickness of plastic sections in the heating zone. Conventional injection moulding die designs and die metals can be used. The injection moulding of Saran is unique. With other commercial thermoplastics, the use of cold die hastens the cooling of the plastic part and shortens the cycle. With Saran the reverse is true. Cold dies produce soft, flexible, amorphous pieces. Rapid hardening is accomplished by heat treatment producing recrystallization. This is done by using heated dies. For normal sections, this permits short cycles. When heavy sections are involved, heated dies allow the section to retain its heat and thus recrystallize rapidly. Under these conditions, Saran can be ejected from the die at temperatures as high as 70 to 80 degrees C. in a strain-free, warp-free, dimensionally stable form. This, of course, promotes very rapid cycles with heavy sections. In fact, mouldings have been produced with $\frac{1}{4}$-in. sections in a 17-second cycle.

Injection-moulded Saran is playing a part in national defence. Many of its applications have been replacements of metals and not other thermoplastics. Comparative tests showed that, in many instances, Saran was the only material that would satisfy the industrial requirements for the replacement of such strategic materials as nickel, aluminium, stainless steel, and rubber in applications requiring chemical resistance.

A few examples of the numerous industrial applications are as follows:—

1. Spray-gun handles — chosen because of solvent and abrasion resistance — replacing aluminium. Here the practice of cleaning the equipment by washing in potent lacquer solvents does not affect Saran.

2. Valve seats—chosen because of freedom from channelling based on abrasion resistance, its seating qualities based on its resilience, and, in some applications, its resistance to corrosive gases and liquors—replacing precision machined metal seats and imported horn seats. In one type of valve, Saran, far outperforming any previous metal seat, showed no air leakage after 15,000,000 cycles of operation.

3. Acid dipper — chosen because of acid resistance and toughness — replacing glass in hard usage where much breakage was encountered.

4. Mouldings for the rayon industry, such as spinnerette couplings, gasket holders, filter parts, nozzle tips, rollers, guides, etc., etc.

In addition to the above uses, Saran is now being

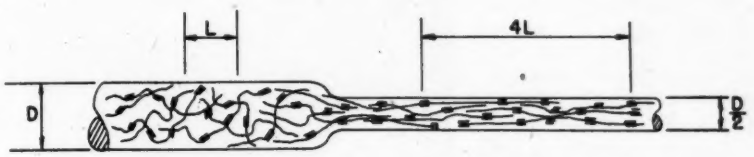


Fig. 4.—Unstretched, unorientated. Tensile 8/10,000 lb. Flexibility—low.

Stretched and orientated. Tensile 30/60,000 lb. Flexibility—high.

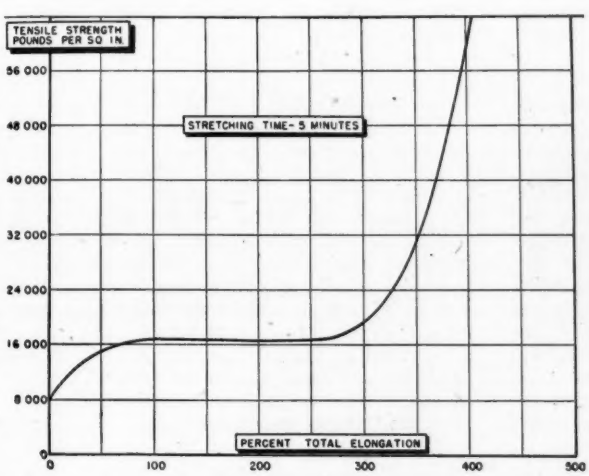


Fig. 5.—Tensile strength of Saran monofilaments plotted against elongation.

called on for the more familiar general type of plastic application. Its good mechanical characteristics, range of attractive colours, and favourable economic outlook point to a promising future for Saran in the injection-moulding field.

Like other thermoplastic materials, Saran can be compression moulded. It differs from the other thermoplastic materials only in that it requires the same selection of metals for the dies as are above listed for hot zones in extrusion equipment. However, like other thermoplastic materials, the economic considerations usually favour injection over compression moulding.

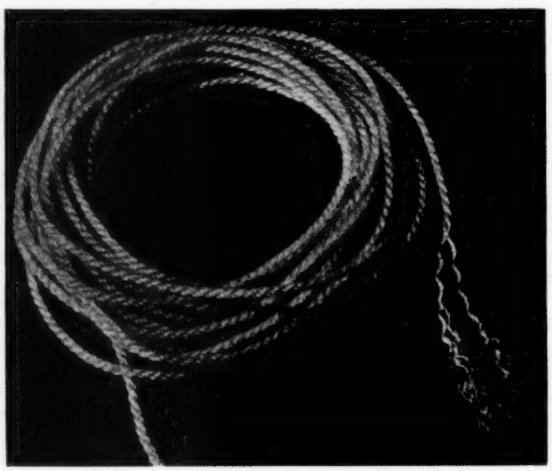
A third method of fabrication, that of crystal orientation, brings out new properties of Saran. The oriented form is produced by extrusion, subsequent plastic deformation, as by stretching, and heat treatment. It is thus possible to obtain long, continuous extrusions of monofilaments, tapes, and other shapes which have exceptional properties. While the method is not complex, it does require special control and careful attention to the techniques involved.

In the production of strong, continuous sections, the plastic must be uniformly heated to a temperature above its crystallite melting point and thereafter cooled below this point. Preferably the material is mechanically formed to a shape similar to that of the section desired before being cooled. One method of fusing and shaping involves the use of a screw-type extrusion machine as described previously. The degree of cooling may be sufficient to reduce the temperature of the fused, shaped mass to about room temperature. The material will remain in this amorphous or super-cooled condition for a sufficient period of time to permit cold-working operations to be carried out. The Saran is now ready for the orientation step.

The orientation process, as diagrammed in Figs. 3 and 4, provides a method of effecting a plastic deformation and partial recrystallization of the shaped, super-cooled material. The method involves an accurately controlled, predetermined rate of withdrawal of the plastic from the extrusion unit. The ultimate size and uniformity of the continuous section is governed by controlling the rate.

The shaped, supercooled material is then elongated under controlled conditions, suitably at room temperature. During this mechanical stretching, there is a partial recrystallization of the material and orientation of the crystallites along the major axis of the strand. The reduction in cross-sectional area is approximately proportional to the elongation produced. The material may be heat treated after or during stretching to affect the degree of crystallization and thus control the properties of the oriented article. After winding and packaging, the plastic strand is ready for use.

The above method will produce orientation in a single direction with resulting uni-directional properties. The resulting tensile strength is a function of the elongation as illustrated in Fig. 5. These uni-directional properties of high tensile strength, great flexibility, long fatigue life, and good elasticity are particularly desirable for small monofilament sections where the load is along the longitudinal axis. In larger, non-circular sections such as tapes, ovals, and semi-circles, the desired degree of transverse orientation can be realized and accompanying transverse properties controlled through the introduction of other factors in the continuous process. For example, a rolling operation incorporated after the quenching step produces some flattening and transverse elongation of the strand with a resultant increase in transverse strength. Other processes involving mechanical or recrystallization control are also available for desired modifications of directional properties. With a range of plastic formulations and the flexibility of the above process, a variety of continuous sections with required properties can be produced.



Example of cord produced from polyvinylidene chloride.

Extruded and oriented sections are now being produced for textile uses, ranging in size from .007 in. to .100 in. in circular monofilaments, and in other shapes having maximum dimensions up to .200 in. These materials have shown adaptability to standard textile operations and have been fabricated by braiding, weaving, knitting and twisting. While many uses now exist for monofilaments in the sizes commercially available, still greater fields await single and multiple fine fibres having the properties of oriented Saran.

Many uses of Saran monofilaments fall in fields formerly supplied by imported natural products, such as hemp, long fibre paper, reed, rattan, horsehair, Spanish silkworm, gut and linen. From the results obtained, it appears that these substitutions will be permanent. A range of typical examples might include:—

1. Filler Fabrics

Saran's extreme chemical resistance suits it for this use. Since it is a thermoplastic, the question of upper operating temperature limits immediately arises. Experiments show that even at a temperature above that of boiling water, Saran still retains half its original tensile strength. Normal strength is regained on cooling.

2. Special Ropes

Saran's high wet strength and its chemical and fungal resistance have directed its use to special ropes and cores for wire ropes.

3. Articles of Apparel

The general attractiveness and range of colour possibilities fit Saran for such apparel accessories as belts, suspenders, woven and multi-coloured handbags, hats, braces, shoes and decorative applications.

4. Upholstery Fabrics

Long life, ease of cleaning, abrasion resistance and flexibility, as well as colour possibilities, have attracted upholstery fabric applications to Saran. Saran in subway transportation seating shows no material wear and appears like new after a hard service period of over a year. Saran upholstery fabric is now being used on train and bus seats, as well as household furniture and automobile seat covers.

In addition to the methods of fabrication so far discussed, there are other operations based on Saran's combination of thermoplasticity and crystallinity, which have been used in forming the plastic. These operations include drawings, forging, blowing, rolling, stamping and welding.

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World's Industry Employs Plastics

GENERAL ENGINEERING

Gears and bearings are now being produced at Lockport, Louisiana, from a tough plastic made from bégasse, the residual fibrous material left after sugar is removed from cane by crushing. The type of binder is not mentioned, but bending strengths of the order of 13,000 lb. per sq. in. have been obtained. The mechanical strength of bégasse has long been known, for the fibre forms a basis material for the production of Celotex and similar building boards. **Displacement of metal by non-metal** goes ahead in Germany. Among the more recent developments, some of which may have been noted previously on these pages, are portable typewriter frames and other components moulded from phenolic resin with wood-flow filler (type S). Standard head lamps for military vehicles have the customary brass cases replaced by plastics. Use of plastics as insulators in electrical machinery has been extended until these materials have now assumed first place in constructional parts such as housings, hand wheels and handles on such apparatus as motor-driven hand drills, polishers and saws. Electrical protection is thus increased simultaneously with increased ease of manufacture. It has been found possible by the skilful use of injection moulded phenolic resin tubes to dispense with insulated wire, bare wire being used in its place. **Jigs and fixtures in laminated plastic** are about one-sixth the weight of equivalent parts produced in cast iron and steel. It is stated that in many German industries the employment of women labour has been made possible only because of the replacement of the usual heavy metal parts by this more suitable ultra-light apparatus. **Highly stressed gears** are, according to Deitrich, writing in "Deutsche Kraftfahrforschung," not suitable objects for manufacturing in plastic materials, the wear resistance of current types being not of a sufficient order, whilst the high elasticity of the material introduces difficulties, although, at the same time, being of some value for resisting shock loads and for vibration damping, Deitrich suggests that if it were possible to protect the tooth flanks of gears by means of thin, strongly adherent layers of plastic or other materials, the silent running of heavily loaded gears could be remarkably improved, owing to reduced tooth friction; simultaneously, overall efficiency of such gears would be increased. **Elimination or reduction of vibration in precision machine tools** is a cardinal aim, especially in the case of grinding machines and those for precision boring and turning. To this end, gears in the spindle drive are, as far as possible, avoided. Nevertheless, a tool-grinding machine recently developed by Schütte of Köln-Deutz has the grinding spindle driven by a pair of bevel gears, the driver being made in laminated plastic. Further to reduce vibration, hypoid gears are used, and the upper bearings are under spring pressure. In this way it has been found possible with a gear drive to carry out grinding operations normally considered impossible with machines of this design. Incidentally, the bevel-gear drive appears to simplify the positioning of the motor on this unit. Vibration damping of honing tools is, according to Schmidt, writing in a recent issue of "V.D.I.-Zeitschrift," successfully achieved by the use of plastic inserts. **Hard-metal-tipped and diamond-tipped** tools for machining of plastics are lines which should be attracting the attention of all interested in cutting operations in these materials. Urgent demands at the moment have placed such tools in short supply, but production facilities are enormously increasing, hence, it is not unreasonable to hope that, after the war, no difficulty will exist in obtaining them. Even apart from the abrasive nature of any fillers used, plastics, in spite of their relative softness, tend rapidly to wear the sharp cutting edges of tools, hence in mass production demanding close limits combined with fine surface finish, diamond tools are the best proposition.

CHEMICAL

Protection of metallic surfaces against chemical attack still constitutes in chemical engineering a major problem which, however, is being largely solved by increased use of specialized plastics. Such material as polyvinylidene (P.C.U.: Vinedur) and polyisobutylene (Oppanol) have extensively displaced solid metallic parts or base metals coated with other more corrosion resistant metals. A past issue of "Chemische Fabrik," for example, describes solid tubular and other fitments in P.C.U. Protective coatings of these materials may be applied to finished steel vessels, the operative surface of which is first of all etched and then locally heated, the plastic being applied in the form of a foil, joints being effected by welding. Such films are entirely free from porosity and may be applied to vessels of any form or shape. Kranich, writing in "Chemische Fabrik," states that polyvinyl chloride and polyisobutylene surpass in corrosion resistance all hitherto known synthetic compounds. They are resistant to acids and alkalis of any concentration, and, up to temperatures of 120 degrees C., are not seriously affected by oxidizing acids. The use of these materials for sealing against sub-soil water for the protection of underground pipes is particularly dwelt on. The resistance of these and similar plastics to alteration by ageing (physical or structural changes) and by chemical attack (formation of ionizable corrosion products, particularly in the presence of copper) focuses attention on their value in high-tension electrical apparatus and cables such as may find application in chemical plant. Although much research has been carried out on the deleterious effects of ionization on the oil-impregnated paper in oil-filled high-tension cables (e.g., formation of copper and lead soaps on those layers in contact with the core and lead sheathing), and on "gumming" of oils due to high operating temperature (e.g., up to 90 degrees C.) at corona, little has been done on the relatively inert plastics in this connection. Even alleged thermionic emission from heavily loaded conductors appears unlikely to affect these highly polymerized chemicals. The fact that certain thermo-plastic resins normally considered brittle at room temperature would be truly plastic at the operating temperatures noted, is significant.

BUILDING

Inscription boards and plates in laminated plastic are not only easy to produce but are highly resistant to wearing and weathering. Urea-resin laminated paper is preferred owing to its especially high resistance to atmospheric attack. Door plates and name plates in this material are widely used in Germany and their application has been extended to signs on buses,

trams, railway coaches and shops. Boards may be produced by the embodying of an already printed sheet on to a laminated plastic backing or by engraving or milling from a prepared sheet built up of several different coloured layers.

ELECTRICAL

Telephone, telegraph and allied equipment constitutes a field already well explored for the utilization of plastics. Wörgerbauer, in a recent issue of "Elektrotechn. Zeit.," discusses the advantages and disadvantages of synthetic resins in various connections. In this department of electrical engineering, instrument plates may be made of moulded plastics if demands on centre-distance tolerance be not too high. With few exceptions, the effects of water absorption and ageing lead to dimensional changes. Thus, in the case of mechanism with sensitive tooth contact calling for the maintenance of centre distances within, say, a thousandth of an inch, plastics, whether in the form of laminated sheet or as mouldings, are not suitable. For general purposes, however, the outlook is better. Shafts may be run directly in the plastic or in pressed steel or brass bushes. Brass has hitherto been principally used for such jobs as this, hence, in changing over to plastics, allowance must be made for the slightly lower values in mechanical properties in the latter material; increased rigidity may be obtained by ribbing, but, unfortunately, the space necessary for this is not always available. Bushes of plastics found early use in this field owing to their insulating properties, and laminated fabric bushes are extensively used to-day. It is recommended that bushes be drilled before pressing in, in order to permit elastic compression. Ageing of the bush material has little effect on the fit or hold of the bush in the case of thin-walled insertions. Accurate fit is obtained by reaming, the holes in the plates being broached to ensure a safe hold. Speed for non-lubricated journals running intermittently is, in the case of plastic bearings, about 20 ft./min., the maximum specific pressure being 2,800 lb./sq. in. In the case of continuously rotating shafts in teleprinters, for example, heat dissipation may become troublesome. However, speeds up to 60 ft./min. entail no specialized designs, even with thick-walled bushes. Plain or helical-toothed gears on telegraphic and other apparatus have, for a long time, been fabricated in laminated plastics; they operate with steel wheels or pinions. Even helical gears with crossed axes give good results when run continuously on teleprinters. Attempts have been made to produce gears of high accuracy by moulding, but, with small-toothed gears, difficulties have been entailed in making sure that the textile-filler particles flow freely into the small tooth spaces. Moreover, the mould itself is difficult to produce, as it features interior teeth which can be produced only by the Fellows method. General indications are, however, that success will eventually be obtained. Tooth wear on moulded gears has been shown to be very satisfactory. Gears in machinery of this type are frequently used for angular drives which do not permit of any easy application of strictly geometrical principles. The fact that this basic inaccuracy has been found no serious disadvantage may indicate that other inaccuracies might be intentionally introduced in order to simplify mould design. Ratchet wheels in laminated plastics have been used in teleprinters even operating at high speed. A correctly designed plastic wheel and its corresponding steel pawl show no undue wear, but a greater fillet radius is required than in the case of bronze or steel ratchet wheels. In this particular type of gear, edge pressure tends to press away the plastic. Cam discs of laminated plastic show great resistance against wear by follower levers, even when these latter actuate with a striking motion; wear cavities produced are, in general, smaller than in the case of metallic cams. A fine oil film, maintained by means of a felt pad pressing against the surface of the cam, and the use of correctly designed and tensioned follower springs, minimizes wear. Those interested in the use of mica as a filler for plastics will be interested in the appearance of "Handbook on Mica," by Ramani Ranjan Chowdhury. This book, containing 344 pages of text, is issued in Calcutta and is obtainable in London through W. Thacker and Co., Ludgate Circus, London, E.C.

AIRCRAFT

The Bendix Dehydrator is now said to incorporate a tough and resilient unit made of Lumarith, the cellulose acetate made by the Celluloid Corporation. **Seaplane Floats** fabricated from laminated resin-impregnated veneers have now been thoroughly tested and found efficient. The new floats which are being fitted to many seaplanes replace aluminium with complete success, and without the fear of salt-water corrosion.

MISCELLANEOUS

Hardness testing by a novel method is described in a more recent issue of "Kunststoff, Technik und Anwendung," by Schmidt-Bisterfeld. An electrically heated cone of sintered tungsten carbide is pressed against the sample and the impression depth measured. Test conditions are, cone of 45 degrees including point angle, with radius 0.5 mm. heated to 20 degrees C. and pressed into the sample. **Mounts for metallographic specimens** are now commonly made in plastics. In America considerable progress has been made, and there, Tracey C. Jarett, who designed a special polish-grinding machine, prefers mounting in phenolic resins in place of transparent thermoplastics. Phenolic resin is said to permit increased polishing speed and to give more satisfactory results. The Fisher Scientific Co., Pittsburg, Pa., have developed a special mounting press for both thermosetting (Bakelite) and thermoplastic resins (Lucite referred to). **Transparent plastic cups** have recently been developed by Dr. Paul H. Harmon, of the Robert Parker Hospital, Sayre, Pennsylvania, for the treatment of arthritic hip joints. These cups, which are already in use in some American hospitals, have been deemed of prime significance as a new surgical appliance in this form of therapy, and the successful treatment of cases of arthritic hip joints has already been reported on in American medical literature. It is claimed that relief from pain is almost immediate after a surgical operation at which the hip is remodelled and a plastic hemisphere placed in the reconstructed joint. The hollow plastic cup replaces the worn and diseased cartilage and acts as a cushion within the joint. Smaller cups have had a limited trial for arthritis of certain joints of the hand, but these appear to be the only joints to which the method is applicable. The cups have been produced from Plexiglas and Lucite and have been subjected to exhaustive tests. Their great value rests in the fact of their being clearly transparent, so that the surgeon may determine the status of the joint by *x*-ray at any future time without difficulty after the insertion of the cups. **Refrigerator ice-cube tray,** moulded in one piece, has been developed by Modern Products and Materials Co. The material employed is stated to be an "oil-modified" cellulose acetate. While the use of such a plastic for this job is surprising, presumably the modification improves water resistance.

Ideas—

By the EDITOR

Our friend Dr. de Bruyne sends us the following note:—"To swell your ideas page I am sending with this letter what aeroplane designers would call a 'mock up' draw pull. The point about it is that it is made from a piece of the extruded 'Rockite' hexagonal tube obtainable in long lengths (at least before the war) from F. A. Hughes and Co., Ltd. This hexagonal tube was sawn up and stuck on the base plate with Ardux. The colour scheme of the enclosed example is, of course, revolting, but the idea of welding up objects from ready-made extrusions and flat sheets is the important point. The quick-setting characteristics of Ardux are just as important for such work as its strength." The idea is seen

Gluing Technique

in the accompanying drawing. Incidentally, I cannot refrain from pulling de Bruyne's leg and telling him that the draw pull looks suspiciously like having been cut from an octagonal extrusion and not a hexagonal one. Also the extrusions are still available from F. A. Hughes and Co., Ltd.

In truth, Ardux appears to have started a very new technique—one which will not only help moulders in their present difficulties, but also in the matter of new designs. In the December, 1941, issue of "The Times Trade and Engineering Supplement," Dr. Yarsley agrees and points to the possibility of building up hollow articles on the lines of chocolate eggs. The hollow spheres used for cistern valves are a perfect instance. Obviously, too, the plastic fancy goods trade after the war will benefit immensely by this material.

My readers will remember that some time ago I published a photograph of a baby's cot, made in transparent cellulose acetate sheet, that is being used in American hospitals and crèches. I was delighted with the idea, especially with that part of it which claimed that transparency gave the nurse a chance to see whether the infant was attempting suicide by swallowing its bottle or plotting against authority.

Not So Hot

I took the idea round to Miss Weston of Treasure Cot, Ltd., in Oxford Street, who is unusually wise and enthusiastic about plastics in children's furniture generally. She thought such a cot a great advance on the wicker-work type which often sticks nasty points into the baby, but on the point of transparency she was scornful. "Obviously designed by a man," she said. "Any woman would tell you that the baby must be made to sleep and the slightest outside movement visible by the baby keeps it awake." I retired somewhat crestfallen.

Thirty thousand of the war-economy "U.L." plastic lighters will be on sale in the shops before long at the Government controlled price of 6s. 6d. each. So the "Daily Express" tells us. There will be three colours, black, green and red, and plenty of spare parts will be available—at 4d. upwards. We are told that the 6s. 6d. is divided as follows:—

That Lighter Again

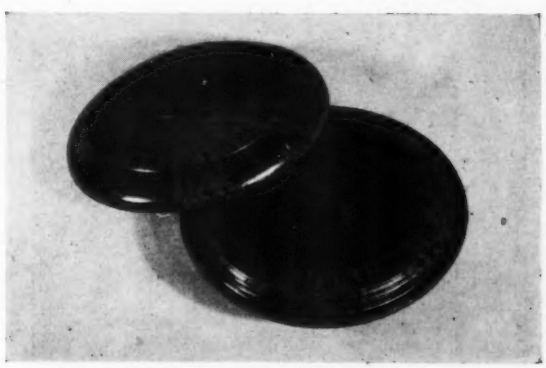
Government Excise	2s. 6d.
Retailer	1s. 6d.
Wholesaler	6d.
Manufacturer	2s. 0d.

Not a bad rake-off for the Government, I must say. Slightly over 38 per cent.

The "Daily Express" also publishes a photograph of one of the infernal machines made by a Mr. W. H. Berry, who got the miracle idea from his daughter. As I said last month, it has a loose screw top for the wick. If this is Mr. Berry's idea of a good design, we recommend him to go to those who have made lighters for years. However, I suppose the trade will make money selling replacements. Why he is getting all this marvellous publicity for a poor thing beats me. I hear the plastics industry is getting down to it and no doubt will produce something better.

It's nice to think that moulders have still us smokers at heart, even during war-time. So here is a sensibly shaped tobacco container conforming to the streamline idea—light, easy to unscrew and more or less airtight. The only fault I can find with it is that although the advertisement says it will also hold a cigarette paper package, the diameter is not large enough to push

New Tobacco Flap



the package in without buckling. This is enough to make the average cigarette paper foam at the mouth. A small cut-out should have been made to accommodate it more readily. It is distributed by Parker Pipe Co., Ltd., and, while I do not know who moulded it, bears the trade mark "Beacon." A worthy piece of work all round—except for the mottle!

INQUIRIES AND ANSWERS

(In Which is Included General Correspondence)

IMPORTANT NOTICE: If inquirers wish to receive replies by post, a stamped and addressed envelope must be included in their letter. Unless otherwise stipulated, it is understood that the submission of a problem to the Editor permits its publication in this journal.

Synthulite Resin

Further to the inquiry by Fireproof Tanks, Ltd., in our December issue, Mr. Salas, of Bakelite, Ltd., informs us that the trade name Synthulite is held by Nilles and Siner, London, W.C.1. This concern makes sleevings, etc., by extrusion, using polyvinyl chloride resin.

Supplies of Cotton Filler

Mr. Perry Backstrom, of "Modern Plastics," has suggested to the writer that I write you with regard to the possibilities of being of assistance to moulding powder manufacturers in England with regard to cotton filler flock or fabric filler. We are at present supplying firms in the United States with several styles of cotton filler flock and fabric filler for high impact strength plastic powders, and are interested in developing the sales of these products in England.

Any information you can give us with regard to the consumption of this product in England, importers interested in handling this product for us in England, concerns to whom we could write direct, or other pertinent data would be sincerely appreciated.

M. A. FOLEY.

Rhode Island. Rayon Processing Co. of R.I.

Optical Graticules

As a manufacturer of optical graticules, it has been my misfortune to have to attempt the production of compass dials on mother of pearl, and since this raw material is exceptionally unsatisfactory in so many ways, I have suggested that engraving be given up, and that some moulding or stamping firm is requested to make the dials out of plastics, the lines being moulded or stamped on the raw material and filled in with black afterwards.

It may be as well to add that the present cost of producing a pearl dial is about 2s. each, about half this being the pearl and the other half being the engraving.

The cost, of course, is nothing like so important as the production, and all the factors in the latter are on the side of the plastic. I have no financial interest in any particular process, and should be very pleased to give all the information in my possesion to any friendly firm who think it is worth its while to go into the matter.

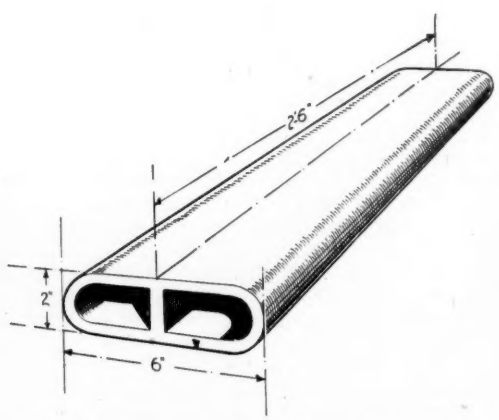
The dials are floated in (I think) iso-butyl alcohol to damp out oscillations rapidly, and the black used for the lines may have to be stoved off at about 150 degrees C., so that these points would have to be taken into account when choosing the plastic for the job. I imagine that a good thermosetting type would be quite satisfactory. C.S.

[EDITOR'S NOTE.—Much as we love tilting at Authority and telling it how plastics are better than anything else, we fear that here we have a bit of work that cannot be surpassed for the job. Before we had received the sample we had imagined that someone in the Ministry of Supply had found a mother-of-pearl mine and was anxious to use the stuff up. However, we were wrong. The circle of mother of pearl (about 1¼ ins. diameter and 10/1000 in. thick) is most beautifully engraved and the material itself is one of the few that could be used. We cannot imagine (a) that any plastic sheet could be moulded or engraved with such accuracy and fineness of detail, and (b) that any plastic would stand up to the damping liquid, whether iso-butyl alcohol or a mineral oil. The value of the mother of pearl would seem to lie in the fact that the material is inorganic, hard and dense, and obtainable in very thin sheets. If a different damping liquid were possible, say, water or glycerine, we might suggest polystyrene, which can be beautifully engraved. As a moulding job, we should not like to attempt it, and there seems no point in blanking and engraving. We should be glad to put those who think otherwise in touch with the inquirer.]

Extrusions for Optical Apparatus

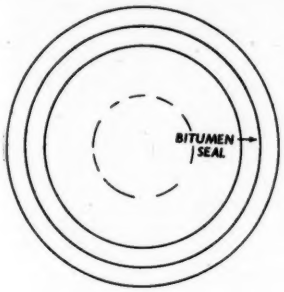
The drawing attached is that of part of an optical instrument and I should like to know if it can be extruded in lengths as shown. The material should be thermoplastic and fairly pliable. Are there any manufacturers who would be in a position to mass produce at the present time? S.F.

Hants.



[EDITOR'S NOTE.—From the mere profile point of view, there is no difficulty in the extrusion of this object. The size, however, is a bit frightening and the chief difficulty would be to prevent collapse of the tube as it issues from the die. In a small tube (the largest we have seen in thermoplastics is about 1 in. diameter) this is carried out with air pressure. We suppose all extruding machines in this country are doing cable covers and, judging from the sizes we have seen, could not be adapted to take such a large die. Inquiries should be made of concerns such as F. A. Hughes and Co., Ltd., Souflex, Ltd., Tenaplas, Ltd., Nilles and Siner, Ltd., etc.]

Plastic Sheet and Film Materials for "Protection" General Wrappings



By
E. E. HALLS

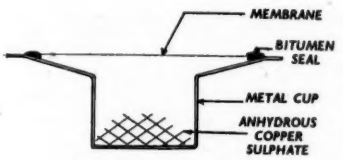


Fig. 1.—Arrangement of membrane on test assembly for moisture permeability determination.

The use of Plastic Sheet as Wrapping has become so widespread that the detailed comparisons of the important property of "moisture-proofness" given below are of fundamental importance.

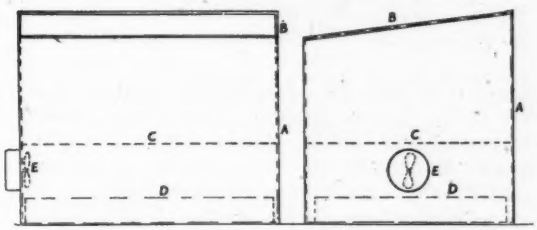


Fig. 2.—Humidity cabinet for moisture permeability tests. A, teak cabinet; B, sloping glass top; C, perforated shelf; D, tray of water; E, slow moving fan.

THE term "wrappings" covers a diversity of types of packs and seals. These utilize an almost unlimited range of materials, often ingeniously adapted, formed or applied; and, in itself, the wrapping usually has many of numerous functions to fulfil. It is interesting, first, to enumerate the outstanding criteria of the general wrapping materials, then to consider the range of basic raw materials utilized, and finally to examine the rôle fulfilled by plastics. This is rather a comprehensive problem, and in the following it is attempted mainly on the basis of one particular property, that of moisture-proofing.

General wrappings mainly embrace film, sheet and card materials, but items such as bottle closures of plastic, e.g., rubber, nitro-cellulose, varnished silk, etc., can conveniently be included. The commodities using them are legion, and the purposes served are often strongly contrasted. Food is wrapped on some occasions to keep it moist (bread, fish), upon others to keep it dry and retain crispness (biscuits, cereals); yet again, protection may be required to prevent other forms of deterioration by dampness (chocolate and confectionery). Articles of clothing, especially shirts and collars and lingerie, use modern packs to permit handling and inspection without damage, and for the retention of freshness and stiffness under storage or display conditions. Items of apparatus, electrical or mechanical, and domestic appliances of utility or ornamentation, are wrapped to protect the surface of metal or woodwork from spoilage of finish. At times a choice may have to be made between added protection to the article with an ordinary wrapping or no protection with a moisture-proof wrapping (e.g., lanoline-greased razor blades in plain paper envelopes or dry blades in a moisture-proof covering). These, of course, are only a few illustrations to show the nature of the field covered.

Briefly listed, the chief criteria for a wrapping material are as under:—

1. Cost. Generally the wrapper has only a temporary rôle to fulfil, and the expense of it appears under the category of "overheads"; hence the material must be relatively inexpensive.

2. Availability. There must be no break in continuity of supply. It must be freely obtainable in the thickness or thicknesses required, in sheet, strip or roll form.

3. Manipulability. The material must respond to the method of application involved, that is, manual, machine or automatic machine, and to any processes of cutting or stamping entailed. It may also have to be capable of embossing or serrating and of taking print or patterns by orthodox methods.

4. Colour. This may be of consequence, and apart from a good natural appearance, colours or multi-colours may be required. These include transparent or opaque.

5. Transparency. Good transparency is necessary when viewing through the wrapper is a fundamental feature.

6. Strength. Maximum mechanical strength, tensile, tear and impact, with minimum thickness, is required. "Stretch" or good elongation are useful characteristics in some applications.

7. Permanence and Inertness. The material should be stable and free from tendencies to "age" and thereby deteriorate. Its initial mechanical and physical properties must be retained. It must be inert and neutral, so that in itself it shows no tendencies to react with the material enclosed; that is, free from acids and alkalis that can react with metal work or damage applied finishes; free from injurious chemicals that can harm foodstuffs. It must likewise be devoid of any odour that might be transferred to the goods, thereby devaluating them.

8. Moisture-proofness. The wrapper needs to possess specific properties in this direction because a product wrapped needs to be kept wet or dry, or it requires to "breathe" to a limited extent, or again it may have to "breathe" freely.

9. General Response to Conditions and Handling. Broadly speaking, the material of the wrapping must

Table 1.—Moisture Permeability Values of Papers and Treated Papers. Values in Mgms. of Water Penetrating

Sample No.	Material	Thickness, in.	Period in Days of Exposure to 100% Humidity Gradient									
			1	2	3	5	7	14	21	28	35	42
1	Blank with metal membrane	0.010	Nil	—	—	—	—	—	—	—	—	Nil
2	Blank with no membrane	—	185	375	530	670	790	960	900	—	—	—
3	Tissue paper, white "acid free"	0.0016	160	325	471	765	910	—	—	—	—	—
4	Kraft paper, brown	0.004	100	197	286	503	687	840	—	—	—	—
5	Kraft paper, brown	0.006	200	390	575	830	860	—	—	—	—	—
6	"Waterproof" Kraft, brown	0.004	276	533	790	920	—	—	—	—	—	—
7	"Hydrated" paper	0.001	88	197	276	444	597	820	—	—	—	—
8	Leatheroid (vulcanized paper), grey	0.006	85	180	257	421	592	835	—	—	—	—
9	Waxed parchment paper, white	0.0011	25	50	73	128	189	365	545	705	800	800
10	Waxed paper, brown	0.0025	50	104	152	260	373	740	800	—	—	—
11	Waxed paper, brown	0.0030	18	38	55	82	109	210	304	395	478	555
12	Waxed paper, brown	0.0035	254	510	775	900	—	—	—	—	—	—
13	Waxed paper, brown	0.005	40	89	132	220	310	590	860	—	—	—
14	Waxed paper, brown	0.008	110	253	400	673	900	—	—	—	—	—
15	Bituminized paper	0.0030	5	11	16	23	31	58	87	130	155	178
16	Bituminized paper	0.0065	9	20	27	44	59	130	192	265	310	380
17	Bituminized paper	0.0075	211	444	645	850	—	—	—	—	—	—
18	Kraft paper impregenated with polystyrene resin solution	0.0080	19	40	53	87	116	250	365	510	617	738
19	Kraft paper spray lacquered with nitro-cellulose lacquer	0.0060	85	165	250	414	575	850	850	—	—	—
20	Varnished paper (linseed oil varnish base), yellow	0.003	7	14	20	34	47	92	138	183	230	275
21	Varnished silk (linseed oil varnish base), yellow	0.004	8	15	22	37	52	110	165	215	270	322
22	Varnished cambric (linseed oil varnish base), yellow	0.005	4	18	11	18	23	45	66	89	110	130
23	Varnished silk (linseed oil varnish base), black	0.004	6	12	17	27	39	83	123	160	200	240

retain a neat, attractive appearance, despite exposure to more or less severe atmospheric conditions, including temperature and humidity fluctuations, and in spite of repeated manual handling. Of these criteria, this article will concentrate upon moisture-proofness.

A note of warning seems warranted at the outset. The quality of moisture-proofness is of fundamental importance in any wrapping material, but this fact does not imply that absolute moisture-proofness is required or is even desirable. This aspect of the subject will be referred to again at a later stage, and meanwhile this characteristic will be discussed purely as a property of the material concerned, and without reference to the product that is to be wrapped, the mode of wrapping and sealing or open folds.

First, some explanation of the evaluation of "moisture-proofness" of materials is required in order to clarify the basis of the test data presented. There are several methods of determining the comparative moisture permeabilities of film materials. They are all based upon the measurement of the quantity of water vapour passing through the material when subjected for a period of time to a humidity gradient, maintained between opposite faces of the material, at a specified temperature. One particular test procedure will be described, with illustrative results recorded upon various materials, and later the results will be discussed to show the mechanism of moisture permeation and the factors upon which it is dependent.

The moisture permeation test used for determining the values referred to herein used a circular test piece of the material sealed to a flanged metal cup containing a drying agent. The specimen was assembled in the following manner:—A continuous ring of melted bitumen was applied to the flange. Two grams of freshly prepared, anhydrous copper sulphate was rapidly introduced into the cup. The circular test piece was then pressed into position on the bitumen seating, and a closing ring of bitumen applied around the upper surface and outer edge. Care was taken to ensure the edge was completely sealed with bitumen and that no apertures were left unsealed. An electric soldering iron was employed to facilitate this operation. The position of the bitumen seal was arranged to leave approximately 1 sq. in. area of test material, through which the passage of water vapour could be studied. This set-up could be weighed initially and at intervals after exposure to 100 per cent. humidity at ordinary temperatures. The humidity was secured in a closed sealed cabinet having trays of water in the base and a slow-moving fan to promote uniformity of atmosphere. The specimens were laid on a perforated tray in this cabinet.

The test assembly is shown in Fig. 1 and a suitable test cabinet in Fig. 2.

Table 2.—Moisture Permeability Values of Various Regenerated Cellulose Sheet Materials. Values Expressed in Mgms. of Water Penetrating.

Sample No.	Material	Thickness, in.	Period in Days of Test Exposure to 100% Humidity Gradient									
			1	2	3	5	7	14	21	28	35	42
1	Blank with metal membrane	0.010	Nil	—	—	—	—	—	—	—	—	Nil
2	Blank with no membrane	—	185	375	530	670	790	960	900	—	—	—
24	Regenerated cellulose film, normal quality	0.0012	165	320	485	800	950	—	—	—	—	—
25	Regenerated cellulose film, normal quality	0.0016	170	360	480	810	950	—	—	—	—	—
26	Moisture-proofed regenerated cellulose film, manufacturer "A"	0.0010	4	8	12	20	29	56	85	110	140	170
27	Moisture-proofed regenerated cellulose film, manufacturer "A"	0.0013	6	12	18	28	38	78	115	148	177	203
28	Moisture-proofed regenerated cellulose film, manufacturer "A"	0.0017	6	13	19	33	47	105	158	195	240	280
29	Moisture-proofed regenerated cellulose film, manufacturer "B"	0.0009	9	18	24	38	53	102	151	202	250	303
30	Moisture-proofed regenerated cellulose film, manufacturer "B"	0.0012	18	37	54	89	121	235	355	472	594	703
31	Moisture-proofed regenerated cellulose film, manufacturer "B"	0.0018	16	31	43	65	87	158	240	308	383	470
32	Moisture-proofed regenerated cellulose film, heat-sealing grade	0.0010	6	12	17	29	41	90	138	180	220	258
33	Material after mechanical, physical or chemical ageing:—											
	Material No. 26 after:—	0.0010										
	(a) Severe creasing		7	13	19	32	44	80	115	140	180	210
	(b) Exposure to dry heat at 60°C. for 1 day		8	15	23	37	50	82	122	160	196	230
	(c) Exposure to dry heat at 60°C. for 42 days		19	43	66	100	140	278	415	553	690	800
	(d) Immersion in distilled water for 1 day		4	8	12	20	29	56	84	108	135	160
	(e) Immersion in distilled water for 42 days		5	9	15	24	33	62	95	120	155	187
	(f) Subjection to cyclic humidity test for 42 days		8	16	25	38	51	100	147	186	223	260
	(g) Immersion in acetone for 1 hour		150	220	290	410	500	610	700	780	860	860
34	Material No. 27 taken from service	0.0013	8	17	26	42	57	116	172	226	274	328
35	Material No. 30 taken from service	0.0012	19	37	56	91	127	247	361	483	593	710
36	Material No. 32 after:—	0.0010										
	(a) Exposure to dry heat at 60°C. for 42 days		25	59	80	142	205	403	610	810	860	860
	(b) Immersion in distilled water for 42 days		6	13	21	34	48	95	142	188	237	285
	(c) Subjection to cyclic humidity for 42 days		9	20	29	50	71	140	215	283	355	420

Surprisingly concordant results are obtained by this method of test. Tests should be conducted in duplicate or triplicate to ensure correctness of conditions, especially with respect to proper sealing. The suitability of the bitumen can be confirmed by using a metal membrane, such as one of 0.010-in. thickness aluminium. Subjected to the test conditions of humidity gradient, such a set should withstand the test indefinitely without absorption, and actual tests extended over six to twelve months revealed no increase in weight, which substantiates that bitumen is a satisfactory material for the closure. Other blank tests can be conducted to establish the significance of the test values. Thus the cup, complete with bituminous ring and charge of anhydrous copper sulphate, but having no membrane in position, indicates the normal rate of absorption of water vapour under the test conditions obtaining. Obviously such a test cannot be run for many days as the absorbing material soon becomes spent. Again, a membrane of ordinary untreated paper may be used, e.g., Kraft packing paper, a tissue or an ordinary "Cellophane," against which to compare the more moisture-proof types.

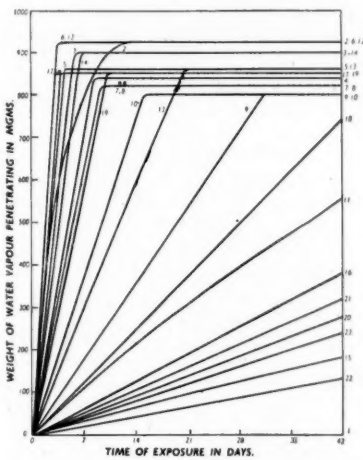


Fig. 3.—Moisture permeabilities of papers and treated papers.

The weight increase of the test set up is dependent upon humidity gradient, temperature, exposed surface area of the membrane, the quantity of anhydrous copper sulphate and its mode of distribution, as well as obviously upon the nature of the membrane itself and the time period of subjection to the test. Some unavoidable errors occur to prevent the relationship between weight increase and time from being entirely linear. In the initial stages of test the membrane itself has to attain equilibrium under the humidity conditions. Hence, it may be some hours before the set-up settles down to its steady maximum absorption. Again, if the test is extended for a considerable period the rate of permeation may fall off somewhat, due to the upper and more exposed layers of copper sulphate having become hydrated. These shortcomings can be overcome in some measure by appropriate modifications to the test. Silica gel can be used as absorbent with some advantage. Again, the humidity gradient can be reversed. That is, a measured quantity of water may be inserted in the cup and the test set-up exposed in a desiccator, thus providing a 100 per cent. to 0 per cent. humidity gradient from inside to outside, as contrasted with this humidity range from outside to inside. This method is rather more accurate, and the accuracy of the humidity gradient can be better assured, but generally it is less convenient to manipulate in practice. The values given show that the method described serves the purpose for which it is designed very well indeed.

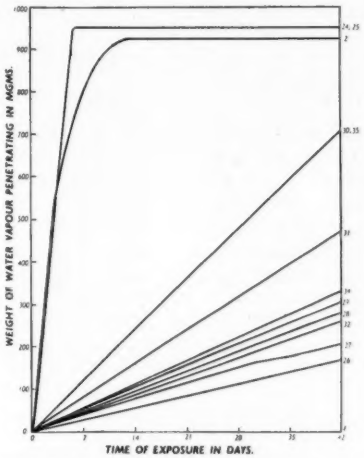


Fig. 4.—Moisture permeabilities of regenerated cellulose films.

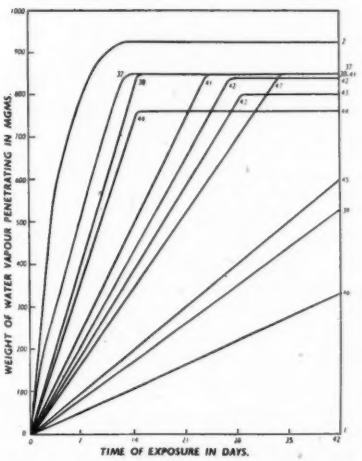


Fig. 6.—Moisture permeabilities of cellulose derivatives.

The ordinary general-purpose wrappings comprise primarily papers and treated papers. The papers include various tissues such as the soft, light but flimsy jeweller's tissue and the heavier M.G. sulphites, and the Kraft wraps of heavier paper. All are generally chemical woodstock base.

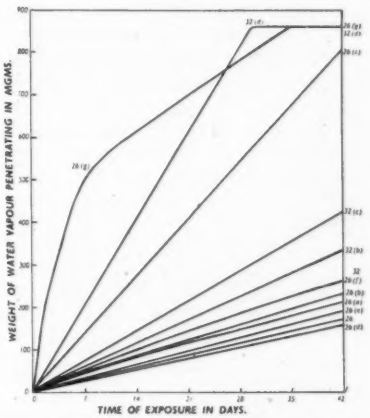


Fig. 5.—Moisture permeabilities of regenerated cellulose films after ageing.

"Moisture-proof" Kraft are available, these generally having a processed surface that apparently involves a starch or dextrine dope; they appear to be designed to resist penetration to liquid water rather than to moisture vapour. Again, parchmentized or hydrated papers, such as the glascines, are obtainable, and these, in the heavier substances, become in effect "vulcanized fibres," e.g., fish paper, leatheroid, etc. None of these products are moisture-proof in the sense of the present discussion. They are much improved by wax or bitumen impregnation and by resinous and varnish treatments, synthetic or otherwise. Fabrics (cotton or silk base) similarly treated have limited applications.

The next group of light wrapping papers is that designated the "regenerated cellulose films." These, in effect, are cellulose dissolved in chemical solutions, such as zinc chloride or cuprammonium, and reprecipitated in film or sheet form. "Cellophane" and Viscacelle are widely recognized examples. These celluloses are not moisture-proof, but in more recent years all the manufacturers concerned have developed

moisture-proof modifications. Furthermore, heat-sealing varieties are available.

Another group of plastic wrapping foils are the cellulose acetates. They have many meritorious features, although, unfortunately, moisture-proofness is not one of them. In the early days of "non-flam" film, thin acetate films were marketed having exceptional qualities of moisture impermeability, but they have long since disappeared. This is to be regretted, and one looks to the future, not only for the straight acetates, but also to the possibilities of the acetate butyrates.

In recent years a rubber hydrochloride film termed Pliofilm has met with much success in America. This success includes both production and usage, and most of the wrapping criteria, including moisture-proofness, are fulfilled. It is, perhaps, proper in this category to include rubber itself.

Established, economic and available materials only have been mentioned and they form a sufficiently wide range for the present purpose. The future may have much in store in the way of improvements, and there are certainly abundant plastic raw materials now extensively manufactured on a commercial basis that give good promise for film and sheet production, e.g., polyvinyl chlorides and polythenes.

The moisture-permeability values of representatives of the groups discussed are summarized in Tables 1 to 4.

Table 1 appertains to the papers and treated papers. Specimens 3, 4 and 5 cover a range of types of paper, and thicknesses, while No. 6 shows the relative position of a so-called "waterproof" variety. All these "plain" papers are closely similar in moisture-proofing quality, viz., highly permeable. Sample 7 is the glascine type and No. 8 the same kind of material in much thicker gauge. Samples 9 to 14 embrace the waxed parchments and waxed Krafts (sometimes referred to in commerce as "oiled" papers). It will be noted that, with the exception of No. 12, they are good; No. 12 actually was very deficient in wax content. This stresses the need for examination of the quality of a material rather than accepting it merely on a description, even though it belongs to a category of materials that, on the whole, are known to be of high merit. Again, Nos. 15, 16 and 17 represent the bitumen-impregnated materials, with Nos. 15 and 16 of excellent quality and No. 17 of negligible moisture-proofing value. Incidentally, this again proved to be a question of the quality of impregnant, Nos. 15 and 16 over a wide range of consignments containing 35 to 50 per cent. of bitumen, No. 17 merely containing 2 to 3 per cent. Obviously this quantity is inadequate.

Sample 18 is of special interest, being a Kraft paper heavily impregnated with plasticized polystyrene resin. Analysis showed the resin content to be 36.5 per cent. Comparison with plain Kraft No. 5, and with the bituminized materials, Nos. 15 and 16, show definitely the beneficial influence of this treatment and its limitations. Sample 19 shows the limited utility of a nitro-cellulose paper varnish; in effect, the sprayed film of cellulose lacquer is far too thin to achieve marked improvement.

To compare and contrast with these treated materials, a truly varnished paper is included in sample 20. This is a thin flexible paper, impregnated and surface-coated both sides with a flexible linseed-oil varnish. It will be noted that this material is exceptionally good. Silks and cambric of similar type are likewise shown in samples 21, 22 and 23, and their moisture-proofing value is undisputed. The results are graphed in Fig. 3.

Table 2 is confined to the regenerated celluloses of different types and origin, and after subjection to artificial ageing tests. Samples 24 and 25, the ordinary grades, are seen to have no claims towards moisture-proofing. Samples 26 and 31 are the moisture-proofed varieties in the normal range of thicknesses and from two manufacturers. Apart from the good moisture-proofing characteristics exhibited, the uniformity in this respect is particularly noteworthy. Sample 32, a heat-healing and moisture-proofed modification, calls for the same high praise. Again, samples 34 and 35, taken from packages in service, are to be commended for the degree of retention of the moisture-proofing qualities. The ageing tests covered by samples 33 and 36 are self-explanatory. It will be noted that moisture-proofed regenerated cellulose withstands severe creasing very well, but that continued dry heat produces some deterioration and the cyclic humidity test deterioration to a lesser degree. Water immersion, however, does not impair the quality. The acetone test was included mainly with the use of adhesives in mind; it will be noted that it is damaging, and consequently adhesives must be chosen discreetly and used with care.

Table 3.—Moisture Permeability of Cellulose Derivative Films. Values in Mgms. of Water Penetrating.

Sample No.	Material	Thickness, in.	Period in Days of Exposure to 100% Humidity Gradient								
			1	2	3	5	7	14	21	28	35	42
1	Blank with metal membrane	0.010	Nil	—	—	—	—	—	—	—	—	Nil
2	Blank with no membrane	—	185	375	530	670	790	960	900	—	—	—
37	Cellulose acetate, clear, colourless	0.0005	120	195	260	380	510	850	850	—	—	—
38	Cellulose acetate, clear, colourless	0.0010	80	125	175	280	400	840	850	850	—	—
39	Cellulose acetate, clear, colourless	0.0010	10	18	28	49	68	178	270	355	435	525
41	Cellulose acetate, clear, colourless	0.0025	60	95	130	182	240	490	738	850	850	—
42	Cellulose acetate, clear, colourless	0.0030	55	90	120	173	220	445	650	840	840	—
43	Cellulose acetate, clear, colourless	0.0050	35	63	90	144	201	411	593	777	800	800
44	Cellulose acetate, clear, colourless	0.0050	95	142	193	280	370	740	760	760	—	—
45	Cellulose acetate, clear, colourless	0.0105	14	30	42	69	97	196	301	399	494	602
46	Nitro-cellulose film (photographic) clear, colourless	0.0045	10	20	26	41	55	115	171	223	277	330
47	Benzyl cellulose, clear, colourless	0.0075	35	65	91	135	182	369	515	802	756	850

The data from Table 2 is graphed for easy reference in Fig. 4 for the regenerated cellulose in the "as received" condition, and in Fig. 5 for the aged samples.

Table 3 gives data on the cellulose ester and ether plastics. It will be seen that the cellulose acetates, on the whole, behave little differently from the plain papers, until a thickness of 0.010 in. is reached. One marked exception is to be noted, namely, No. 39, an 0.0010-in. material produced during the earlier years of non-inflammable film production. It will also be observed that the two samples in 0.005-in. thickness, from different sources, behave quite differently.

The nitro-cellulose film (sample No. 46) is included in the table because dopes yielding a similar film composition are employed for bottle seals.

The values from Table 3 are graphed in Fig. 6. Apart from the exceptions to which special attention has been called, there is some indication that impermeability is a direct function of thickness with the particular cellulose acetate used for the tests.

(To be continued.)

PRODUCTION NEWS

Raw Materials, New Plant, Works Organization, Control Apparatus, Research, Personal and Trade Notes

PLASTICS CONTROL

The following letter has been circulated to cellulose-acetate moulders by the Plastics Controller:—

It has been brought to my notice that some misunderstanding exists as to the definition of Cellulose Acetate Moulding Powders covered by the Control of Plastics (Nos. 1 and 2) Orders. I have, therefore, to inform you that Cellulose Acetate Moulding Powders are, for the purposes of these Orders, deemed to include any off-cuts or scrap pieces of Plastic materials made from Cellulose Acetate from which articles are subsequently produced by injection or compression moulding.

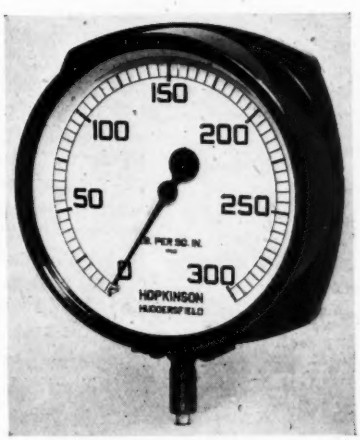
In effect, a licence granted to you covering the manufacture of a specific number of articles covers the consumption of moulding powder—including that derived from rejects and from runners, sprue or flash produced during the course of moulding and normally reworked during the run—only up to the total number of articles stated on your application. Any excess material so derived must be the subject of a fresh licence application and must not be disposed of or consumed except under the authority of a licence issued by this Control. It is also necessary for you to apply for licences to acquire and consume such material if you wish to obtain any from other sources, and to apply for licences to consume any of your own stocks of such materials.

L. P. B. MERRIAM,
Great Burgh, Controller
Epsom. (Plastics Control).

SISAL FIBRE suitably impregnated with resins (Durez phenolics) is now being employed for the production of high-impact mouldings, e.g., gears, bearings, abrasive disc hubs and backs, and mechanical parts generally. The plastic raw material is being marketed in the U.S.A. by the Columbian Rope Co. under the name of Co-Ro-Lite. An interesting application of a Co-Ro-Lite modification is as a sander pad used as a backing for an abrasive-coated sanding disc. Before the Co-Ro-Lite pad was developed, there were in use pads of wool felt, backed with a reinforcing plate and assembled with a threaded die-cast centre by nuts and bolts, or moulded rubber pads with metal inserts. The objectionable features of such arrangements have been met by moulding a pad having different characteristics in contiguous portions from vegetable fibres, using the same heat and pressure in the mould. There are two different bonding materials used in the pad, the centre or hub being vegetable fibres impregnated with a thermosetting resin, and the outer section being of vegetable fibres impregnated with a compounded latex, resulting in a rigid hub centre and a resilient, flexible outer circular section.

NEW STEAM-PRESSURE GAUGE.—An interesting example of the extent to which plastic mouldings are being used in the engineering and allied industries is the fact that Hopkinsons, Ltd., have now placed on the market steam-pressure gauges with casings of this material. The gauges are standardized in sizes of 4 ins., 7 ins. and 10 ins. diameter, the casing being constructed of a strong, high-grade quality moulding, black in colour, constituting an extremely neat job, most distinctive in appearance, especially also as much attention has been paid to the dial marking. In this connection, a style of numeral is employed which enables readings to be taken easily from a considerable distance without having to use unduly large figures.

The new type of gauge is particularly suitable for the panel mounting of instruments, now coming more and more into use for the control of steam boiler plant, not only in electricity stations, but also in medium-sized industrial establishments. For fitting on such control panels, the gauge merely requires to be provided with four bolt distance pieces and a flange ring.



OIL - RETAINING BRONZE BEARINGS.—In connection with the operation of many types of plant and equipment, including, for example, line shafting, electric motors, and electrically driven fans and pumps, one of the difficulties is efficient lubrication of bearings. Quite apart from the considerable net cost of both material and labour involved in supplying oil and grease by means of lubricators, and the damage and general annoyance due to leakage, in many cases the bearings are inaccessible as a practical proposition.

The remedy is the use of self-lubricating bearings, and pioneers and specialists in this field are the British Bound Brook Bearing Co., of Witton, Birmingham, with their special "Compo H" oil-retaining bronze, which contains in the pores 25-30 per cent. by volume of lubricating oil. Consequently bearings of this type will run noiselessly and efficiently for years without lubrication. This special bronze has the chemical composition 88.0 per cent. copper, 9.7 per cent. tin, 1.4 per cent. graphite, and 0.9 per cent. other material, and is made by very high-pressure die-pressing of the pure electrolytic metals in the finely divided condition. Under these conditions the metal is porous because of the micro-cells or spaces between the particles, and on immersion in oil absorbs 25-30 per cent. by volume. Consequently the metallic bearing always has a film of oil at the surface, and as the pressure and temperature varies, as in a bearing, the oil exudes or recedes, giving complete continuous self-lubricat.on under all conditions.

B.X. PLASTICS, LTD.—Owing to the great increase in business and the need for increased accommodation, B.X. Plastics, Ltd., sales offices will be transferred from February 1, 1942, from their present address at Larkshall Road, Hale End, E.4, to Higham Station Avenue, South Chingford, E.4, where all inquiries and matters relating to sales should be sent. The new telephone number (already in operation) is Larkswood 4491. The registered offices still remain at Larkshall Road, Hale End, E.4, where all accounts and matters other than sales should be sent. The most convenient way to reach the new address is by train from Liverpool Street, L.N.E.R., to Hoe Street, Walthamstow, then by trolley-bus to Higham Station Avenue.

Resinoids and Other Plastics as Film Formers

By B. J. BRAJNIKOFF, Consulting Electrical Engineer

IV.—The Structural Properties of Organic Coatings

A GREAT amount of work that has been accomplished lately by various investigators in the field of high polymeric systems proved that insoluble and infusible (or difficultly fusible) high molecular compounds may be obtained by means of either polymerization or the condensation reactions.

The formation of insoluble infusible interpolymers cannot be connected solely with the molecular magnitude, since Staudinger succeeded in preparing very high polymers, namely, polystyrene, with molecular weight of the order 600,000, which were soluble swelled.

Attempts to correlate high molecular weight and particular molecular configurations with infusibility, as made by Mark and some other workers, have also been unsuccessful. Hence it appears that the only interpretation of insolubility and infusibility of such polymers can be conceived in terms of the extent of reticulation, or interlacing of filamentary molecules by cross linkage.

In some respect this process is analogous to the familiar influence of vulcanization on rubber.

Just as the industrial application of rubber was rendered possible only by a radical modification in many of its physical, mechanical and chemical characteristics, consequential to the discovery of vulcanization, so also a priori may be expected the opening of new channels for utilizing of polymer resins in the event of producing the retiform molecules of the cross-linked type.

Accordingly, it must be expected that products in this case will display a definite improvement in heat resistance, which, as a rule, is not very high in ordinary polymers. Certainly there would be a great increase in resistance to the action of organic solvents.

The literature on the subject is very meagre, giving no information as to the technological aspects or the theory of the formation of three-dimensional molecules, and, above all, contains no adequate experimental data that would afford the foundation for any general conclusions.

The only more or less detailed account relates to Staudinger's[10] research on interpolymerization of styrene with divinylbenzene, which plays here the rôle of "vulcanizer." Polystyrene, as a linear polymer, is soluble; but in presence of a minute quantity of p-divinylbenzene the three-dimensional interpolymer, built up by cross-linking of the polystyrene chains with p-divinylbenzene bridges, becomes insoluble.

Another notable work belongs to Norrish and Brookman,[11] who endeavoured to set up a theoretical basis for the conditions governing the formation of three-dimensional molecules.

Formation of Three-dimensional Macromolecules

It would be a mistake, however, to assume that the chemistry of three-dimensional polymers is limited by these two types of reaction, polymerization and condensation. In the process of cross-linking of extended chains we are dealing with intricate reactions of condensation of chain polymers, and combination of the "linking" molecule or atom with the double bonds of the macromolecule.

The analysis of experimental data in this field permits the following classification of reactions for the production of three-dimensional molecules.

A.—Formation of three-dimensional macromolecules by polycondensation.

(i) Formation of three-dimensional products by the polycondensation of homogeneous molecules.

As yet this type of reaction that led to the formation of three-dimensional products has been studied but little.

The examples of such reactions are: the formation of infusible polyglycerides and the preparation of insoluble polyanhydrides of alkylorthosilicic acid. The primary condition for realizing these reactions is that the number of functional groups must not be less than three.

(ii) Formation of three-dimensional products by polycondensation of heterogeneous molecules.

This type of reaction deals with the derivation of three-dimensional molecules by the condensation interaction between the functional groups of various molecules, whose chemical nature is different. These reactions are exemplified by: the formation of insoluble alkyd resins, the preparation of insoluble products of condensation of dibasic acids and polyamines. The condition necessary far producing three-dimensional molecules of this type is that the number of functional groups of one of the components taking part in the reaction should not be less than three, and of the second constituent—minimum two.

B.—Formation of three-dimensional macromolecules by polmerization.

(iii) Formation of three-dimensional molecules by the polymerization proper.

This class of reaction includes the formation of insoluble polymers by polymerizing components containing at least two active double bonds, i.e., compounds of a general formula $X(CH = CH_2)_2$; for example, the derivation of β-rubber by polymerizing butadiene, the insoluble polymers of hexatriene, etc.

(iv) Formation of three-dimensional molecules by inter-polymerization.

This method of synthesizing three-dimensional polymers is of extremely great practical importance, since it allows the production of insoluble and infusible products. This group of syntheses comprises the preparation of insoluble co-polymers of styrol, polyvinylacetate, polymethylvinylketone, polyacrylic and polymethacrylic esters, with divinylbenzene. The imperative condition for performing such a reaction is that one of the constituents participating in the cross-polymerization should have the strucure $X(CH = CH_2)_2$, i.e., its molecule must contain at least two active double bonds.

C.—Formation of three-dimensional macromolecules by interlinking of chain polymers.

(v) Formation of three-dimensional molecules by the condensation "linkage" of chain polymers.

This type constitutes a very large group of reactions, the mechanism being by binding neighbouring chains at separate discrete points, with the evolution of a three-dimensional system; they encompass the formation of such superpolymers as the insoluble cellulose esters (possibly the cellulose itself is built up in this way), the conversion of resol resins into resites and the like. The condition for producing three-dimensional molecules by the process of this nature is the presence in the polycondensate of sufficiently reactionable functional groups ($-NH_2$, $-OH$, $-CONH_2$, $-CONH$, $-COOH$, etc.), and a minimum of two groups in a molecule of the interlinking substance.

(vi) Formation of three-dimensional molecules by poly-condensation linkage and by addition reaction.

The reactions of this type are very numerous. They include first of all the vulcanization of rubber, rubber ageing, oxidation of drying oils, etc.

The prime condition for producing reactions of this class is the presence of double bonds in a molecule of one or another polymer, in contact with the molecules of a substance capable of vigorous reaction with double bonds, the valency of which is at least two (e.g., oxygen, sulphur, selenium, etc.).

The presence in reactions of this nature of extremely small quantities of cross-linking molecules is sufficient for inducing the formation of three-dimensional polymers. Thus 0.01 per cent. of dichlorhydrin is enough to effect the cross-linkage of cellulose chains.

The explanation of this powerful action of minute additions of ingredients resides in the consideration that in the case of filamentary molecules the presence of a negligible number of "bridges" between them is adequate in order to impart to the resultant structure the properties of three-dimensional products.

Hence the basic criterion, which distinguishes the high polymers from low molecular compounds, may be defined as the ability of the former to modify drastically their physical and chemical properties through interaction with small amounts of substances that are specially active inductors of three-dimensional retiforms.

If this concept be adopted as basic, then it follows that phenol-formaldehyde resins, amino-plastics and alkyds fall into the category of low molecular compounds, since these products yield three-dimensional molecules under the action of relatively large quantities of cross-linking reagents.

Important Developments

The phenomenon of the formation of three-dimensional molecules in the process of the cross-linking polymers of diene hydrocarbons (rubbers) has been studied on a comprehensive scale. The building up of three-dimensional insoluble molecules of rubber is observed not only during the vulcanization process, but is present in many other related reactions, such as rubber ageing, derivation of β-rubber, production of insoluble rubber polymers, etc.

The phenomenon of ageing, i.e., the passing of rubber into an insoluble state under the prolonged action of oxygen, is evidently due to the building of oxygen bridges between chain polymers.

In the production of three-dimensional molecules by polymerization and co-polymerization proper should be noted the work of Staudinger and Heuer[12]; they were the first to carry out and study in detail this interesting reaction. These investigators found that in presence of even a negligible amount, e.g., 0.01 per cent., of ρ-divinylbenzol, styrol forms insoluble and infusible polymer, differing from the usual polystyrol by immunity to swelling in so many organic solvents.

Recent years are marked by the attention devoted to developing the insoluble polymers of acrylic and methacrylic acids and their esters. It has been suggested to use the following substances to play the rôle of a second component in this interpolymerization reaction: divinyloxide, divinylketone and p-vinylpropenylbenzol.

The problem of formation of three-dimensional molecules by the cross-polymerization has been extensively studied by Norrish and Brookman[11] by examining production of insoluble polystyrols and polyacrylates.

Selecting for cross-linkage of chain polymers various derivatives of a general formula $X(CH=CH_2)_2$: divinylacetylene, divinylsulphide, divinylsulphone, hexatriene, divinyl, diallyl, divinyl ester and divinylsulphoxide, they have found that three-dimensional molecules were not always formed.

All the resulting co-polymers in appearance are undistinguishable from pure polystyrols or polymethylmethacrylates, differing only by the decrease in solubility and fusibility.

These studies have enabled the authors to arrive at the following interesting conclusions:—

1. The duration of a process greatly varies, depending on the composition of the reaction mixture.

2. The activity (the minimum amount of a reagent that is necessary to form an insoluble polymer) of examined divinyl compounds diminishes in the order as enumerated above, namely: divinylacetylene $>$ divinylsulphide $>$ . . . etc.

3. With a higher concentration of a divinyl derivative, the velocity of the polymerization decreases.

4. Taking into account the analogy of the results observed in co-polymerization of the above reagents with styrene, on the one hand, and with methylmethacrylate, on the other, the authors concluded that the ability to form three-dimensional interpolymers in the cross-polymerization of ethylene (vinyl) derivatives of a general form (difunctional ethylene derivatives: styrol, methylmethacrylate): $R-CH=CH_2$, with divinyl (tetrafunctional) compounds of a general structure: $X(CH=CH_2)_2$, (where X is $-O-$, $-S-$, $-C\equiv C-$, $-CH=CH-$, etc.), depends on: the temperature, the character of the group X; the character of the group R. By the character of the group the authors mean the degree of the electrostatic influence of a group upon the polarizability of the double bond.

Accordingly, the formation of three-dimensional macromolecules is determined by the following factors: (1) the functional structure of reacting molecules, (2) the degree of polarity of double bonds, (3) steric hindrances caused by: (a) greater value of group R compared to X, (b) solvation of group R, and (c) the ability of chain polymers to build meandrine forms which impede the cross-linkage of various chains.

Thus, if $X < R$, i.e., if the formation of three-dimensional lattice is hindered, there is no ground to suppose that in the planes perpendicular to orientation of group R the building of retiform ceases, but such molecules will be two-dimensional structures and, consequently, soluble.

Hence the conclusion that the approximate conditions that favour the formation of two-dimensional polymers are: (1) a sufficient polarity of double bonds of ethylene and divinyl components, and (2) appreciably smaller value X in comparison with R.

Even still greater scarcity of data on two-dimensional molecules prevents their evaluation as film formers.

None the less, there is reason to expect that they

should be characterized by: (1) increased viscous properties of concentrated solutions, and lowered viscosity in dilute solutions; and (2) the viscosity of concentrated solutions in the case of two-dimensional polymers should vary but little with temperature.

Experimental Verification

According to Norrish and Brookman, the fundamental factor permitting the formation of three-dimensional macromolecules is the polarity of the group X in the divinyl derivatives and the resulting distribution of charges in the compound chosen for reaction.

However, the Norrish-Brookman hypothesis becomes too narrow if the range of cross-linking substances is widened.

In particular, as demonstrated recently by Rutovsky and Zabrodine[13] in their researches on polyallylmethacrylate and its co-polymers, diallyl ether does not give three-dimensional molecules.

In the opinion of these authors, special importance should be attached to factors of space arrangement and steric hindrance. With the object of verifying the above view, these workers have subjected to testing, as potential cross-linking components, various substances of similar molecular weight, but different in structure.

Their comparative experiments on the formation of three-dimensional molecules showed that the controlling factors are much more complicated than has been stipulated by Staudinger or by Norrish and Brookman.

The comparison in the behaviour of allyl alpha-methacrylate $CH_2 = C(CH_3).COOCH_2.CH = CH_2$ with diallyl ether $(CH_2 = CH - CH_2)_2 O$ is extremely interesting. Whereas the first forms three-dimensional polymers very readily, the latter does not yield them at all. Apparently, the second reagent gives co-polymers of the ordinary type, which is at variance with the Norrish-Brookman hypothesis.

Also, no three-dimensional molecules can be obtained from derivatives of the form

$$CH_2 = CH - C(OR) = CH_2$$

by interpolymerization with methyl alpha-methacrylate.

The fact, as established by Rutovsky and Zabrodine, that three-dimensional molecules are formed by cross-polymerizing methyl methacrylate with allyl ether of methacrylic acid, is new.

The interpolymers of this nature possess a number of very valuable properties, being distinguished by high impermeability to water, great resistance to the action of oils, benzene, alcohol, and other solvents, and also, with softening points well above 200 degrees C.

Pure allyl methacrylate polymers are brittle.

Experimental Conditions

The polymerization process may be effected by the usual methods, but it is of importance to mention here an aspect, which is likely to lead to marked advance in the treatment of resulting products, which procedure is also novel. It is the use of powdered cross-polymers, formed by emulsion polymerization, as moulding powders as well as coating compositions.

These polymers obtained in the form of globules (controllable) are eminently suitable for compression and injection mouldings, withstanding temperatures well over 200 degrees C. without softening and resistant to solvents like co-polymers produced by other methods.

The allyl ether of alphamethylacrylic acid required for interpolymerization may be easily obtained from methyl methacrylate by alcoholysis[14].

The noteworthy feature of the experiments is that of all examined substances only allyl methacrylate led to the formation of three-dimensional products.

The experimental conditions were as follow:— Methyl methacrylate has been polymerized with diallyl ether in sealed tubes kept at 65 degrees C. for 60 hours without a catalyst, and 8 hours in presence of 0.5 per cent. benzoyl peroxide.

The polymerization of pure allyl methacrylate without catalyzer at 60 degrees C. for 60 hours has yielded a transparent water-clear product, which did not soften at 240 degrees C., and did not dissolve or swell in acetone, chloroform, dichlorethane, and ethylacetate.

By catalyzing with 0.51 per cent. of benzoyl peroxide, kept for 8 hours at 65 degrees C., allyl methacrylate gives analogous transparent, perfectly colourless co-polymer, unaffected by 250 degrees C., insoluble and non-swelling, but very brittle.

The same mixture of monomers has been polymerized by the emulsion method in a 2 per cent. solution of coconut oil soap, in presence of 0.5 per cent. benzoyl peroxide, at 80 degrees C. in two hours.

No insoluble products yielded the cross-polymerization of methyl methacrylate either with methoxydivinyl, or with propyloxydivinyl compounds.

Utilization

Thus, under the conditions as described above, the interpolymerization of methyl methacrylate with allyl methacrylate yields in all cases insoluble and infusible polymers; the resultant product being of the type of organic glass, with almost any desired index of refraction, and capable of transmitting an appreciable amount of ultra-violet radiation, great resistance to high temperatures and immunity to organic solvents, combined with the general chemical stability.

The application of coating and impregnating or cementing compositions may be effected entirely dispensing with costly solvents, by emulsifying a methacrylate in water or by means of hot melts, obtaining fast drying, colourless, tenacious and durable films.

By taking advantage of the polymerization by emulsion method, yielding highly mouldable powdered polymers, the range of utility of products may be greatly extended.

For instance, they can be used directly for innumerable coating and lining operations in situ by means of any spraying apparatus, such as the dual purpose Schori gun, to form protective coverings, membranes or diaphragms in conjunction with any rigid or flexible base, metal, wood, paper, leather, etc.

By utilizing the many outstanding properties of methacrylates, namely, low specific gravities, adhesive power, wide compatibility with multiplicity of modifying agents, e.g., rubbers, resins, plasticizers, oils, dyes, etc., a large variety of superior materials may be prepared, from highly mobile film-forming systems to resilient masses, where the æsthetic and utilitarian effects are combined, thus rendering them usable for speedy and efficient impregnating processes, for electrical and thermal insulation, for the making of cold curved light surgical instruments, especially of "boilable" and sterilizable type, and numerous other applications.

(To be continued.)

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